STRUCTURAL CHEMISTRY
ISSN 2053-2296

A ladder coordination polymer based on Ca^{2+} and (4,5-dicyano-1,2-phenylene)bis(phosphonic acid): crystal structure and solution-state NMR study

Nutalapati Venkatramaiah,[a] Ricardo F. Mendes,[b] Artur M. S. Silva,[a] João P. C. Tomé[c,a] and Filipe A. Almeida Paz[b]*

[a]Department of Chemistry, QOPNA, University of Aveiro, 3810-193 Aveiro, Portugal, [b]Department of Chemistry, CICECO–Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal, and [c]Centro de Química Estrutural, Instituto Superior Tecnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal. *Correspondence e-mail: filipe.paz@ua.pt

Received 4 June 2016
Accepted 29 July 2016

Edited by D. S. Yufit, University of Durham, England

Keywords: ladder coordination polymer; calcium; bis(phosphonic acid) ligand; crystal structure; solution-state NMR study.

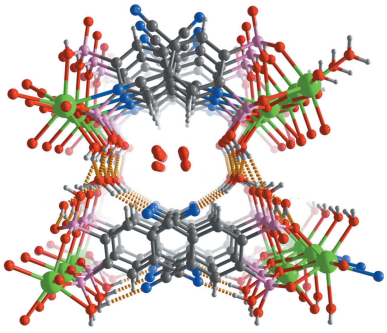
CCDC reference: 1496849

Supporting information: this article has supporting information at journals.iucr.org/c

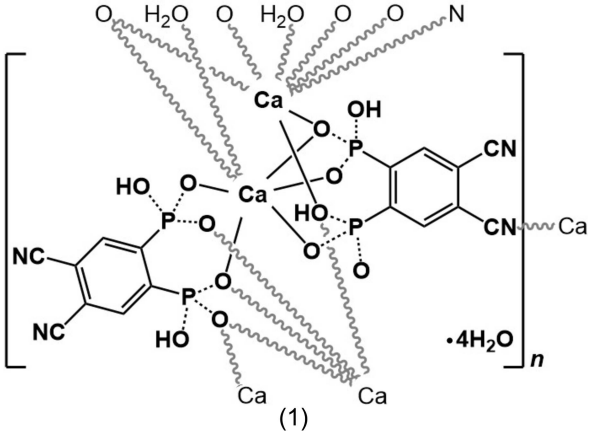
The preparation of coordination polymers (CPs) based on either transition metal centres or rare-earth cations has grown considerably in recent decades. The different coordination chemistry of these metals allied to the use of a large variety of organic linkers has led to an amazing structural diversity. Most of these compounds are based on carboxylic acids or nitrogen-containing ligands. More recently, a wide range of molecules containing phosphonic acid groups have been reported. For the particular case of Ca^{2+}-based CPs, some interesting functional materials have been reported. A novel one-dimensional Ca^{2+}-based coordination polymer with a new organic linker, namely poly[[diaqua[μ_4-(4,5-dicyano-1,2-phenylene)bis(phosphonato)][μ_3-(4,5-dicyano-1,2-phenylene)-bis(phosphonato)]dicalcium(II)] tetrahydrate], $\{[Ca_2(C_8H_4N_2O_6P_2)_2(H_2O)_2]\cdot 4H_2O\}_n$, has been prepared at ambient temperature. The crystal structure features one-dimensional ladder-like $^1_\infty[Ca_2(H_2cpp)_2(H_2O)_2]$ polymers [H_2cpp is (4,5-dicyano-1,2-phenylene)bis(phosphonate)], which are created by two distinct coordination modes of the anionic H_2cpp^{2-} cyanophosphonate organic linkers: while one molecule is only bound to Ca^{2+} cations *via* the phosphonate groups, the other establishes an extra single connection *via* a cyano group. Ladders close pack with water molecules through an extensive network of strong and highly directional O H···O and O H···N hydrogen bonds; the observed donor acceptor distances range from 2.499 (5) to 3.004 (6) Å and the interaction angles were found in the range 135 178°. One water molecule was found to be disordered over three distinct crystallographic positions. A detailed solution-state NMR study of the organic linker is also provided.

1. Introduction

In recent decades, the preparation of coordination polymers (CPs) based on either transition metal centres or rare-earth cations has grown considerably. The different coordination chemistry of these metals allied to the use of a large variety of organic linkers has led to the amazing structural diversity encountered in the literature, with some of the materials also exhibiting applications ranging from gas sorption (Zhai *et al.*, 2016) to catalysis (Mendes *et al.*, 2015) and photoluminescence (Yang *et al.*, 2016). Most of these compounds are based on carboxylic acids or nitrogen-containing ligands. More recently a wide range of molecules containing phosphonic acid groups have been reported. Mixing O- and N-donor atoms in the same ligand is less frequent in the design of novel CPs, as revealed by a search in the Cambridge Structural Database (CSD; Allen, 2002; Groom *et al.*, 2016). Moreover, restricting the search to the use of *s*-block elements yields a much smaller subset of structures.



For the particular case of Ca^{2+}-based CPs, most of the known reports are based solely on a structural description of the obtained networks (Stock & Bein, 2004; Demadis *et al.*, 2009). There are, however, some interesting publications on functional materials. Bishop and co-workers (Bishop *et al.*, 2003) studied the effect of a Ca^{2+} CP in cement hydration inhibition. This polymer acted as a retardant in the setting time of liquid cement, a feature of great importance in the oil industry. In the field of fuel-cell research, Liang and co-workers (Liang *et al.*, 2013) prepared a layered Ca^{2+} CP which shows promising results as a proton conductor. While the material itself has no outstanding proton conduction, this property is greatly increased when incorporated into a polyvinylpyrrolidone (PVP) membrane.



(1)

We report herein the preparation of a new ladder-type CP based on Ca^{2+} cations and anions of (4,5-dicyano-1,2-phenylene)bis(phosphonic acid) (H_4cpp), a novel organic ligand for which we also report the synthetic and structural details (obtained by solution-state NMR). The preparation and structural characterization of this molecule were found to be far from trivial and a detailed NMR study is given. The polymeric material, *i.e.* $\{[Ca_2(H_2cpp)_2(H_2O)_2]\cdot 4H_2O\}_n$, (1), was assembled under atmospheric conditions by a simple and sustainable slow-evaporation method. To the best of our knowledge, this constitutes only the second reported Ca^{2+}-based CP based on a cyanophosphonate or an aminophosphonate linker, with the first being that of Schmidt *et al.* (2011).

2. Synthesis and crystallization

Chemicals were purchased from commercial sources and used without any further purification steps. Tetraethyl (4,5-dicyano-1,2-phenylene)bis(phosphonate) was prepared according to the published procedure of Venkatramaiah *et al.* (2015).

2.1. Synthesis of (4,5-dicyano-1,2-phenylene)bis(phosphonic acid) (H_4cpp)

Tetraethyl (4,5-dicyano-1,2-phenylene)bis(phosphonate) (200 mg, 0.5 mmol) was placed in a 25 ml round-bottomed flask and 6 *M* HCl (10 ml; Analytical Reagent Grade, Fisher Chemical, 27%) was added. The reaction mixture was kept under uniform stirring at 363 K for 6 h, and was then cooled to ambient temperature and the solvent removed under reduced pressure. The obtained viscous oil was precipitated by addition of acetone. The white precipitate was filtered off and dried under vacuum to give (4,5-dicyano-1,2-phenylene)bis(phosphonic acid).

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Ca_2(C_8H_4N_2O_6P_2)_2(H_2O)_2]\cdot 4H_2O$
M_r	760.40
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	180
a, b, c (Å)	16.4384 (11), 25.2929 (18), 6.9599 (5)
β (°)	91.493 (3)
V (Å^3)	2892.8 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.70
Crystal size (mm)	0.10 × 0.06 × 0.01
Data collection	
Diffractometer	Bruker D8 QUEST
Absorption correction	Multi-scan (*SADABS*; Bruker, 2001)
T_{min}, T_{max}	0.665, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27705, 5266, 4050
R_{int}	0.065
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.133, 1.12
No. of reflections	5266
No. of parameters	437
No. of restraints	17
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 10.5068P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.11, 0.46

Computer programs: *APEX2* (Bruker, 2012), *SAINT* (Bruker, 2012), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *DIAMOND* (Brandenburg, 1999).

2.2. Synthesis of $\{[Ca_2(H_2cpp)_2(H_2O)_2]\cdot 4H_2O\}_n$, (1)

H_4cpp (29 mg, 0.1 m*M*) was dissolved in methanol (4 ml) and calcium hydroxide (1 ml, 22.2 mg, 0.3 m*M*; Sigma Aldrich, puriss p.a. ≥96%) was added slowly. The resulting mixture was stirred at ambient temperature for 10 min until a uniform mixture was obtained. The resulting solution was allowed to evaporate slowly at ambient temperature. White crystals of (1) were obtained after one week, harvested manually, filtered, washed with water and finally dried at ambient temperature.

2.3. Structural characterization of H_4cpp (see the *Supporting information* for the spectra)

In DMSO-d_6, ^{1}H NMR (300.13 MHz): δ 8.05 (*dd*, J = 9.0 and 8.0 Hz, 2H, ArH), 7.13 (*t*, J = 50.6 Hz, NH_4^+), 4.51 (*br s*, POH and H_2O). ^{31}P NMR (121.49 MHz): δ 9.77 9.38 (*m*, 2P). ^{13}C NMR (75.47 MHz): δ 144.8 [*dd*, $^1J(^{13}C\ ^{31}P)$ = 161.5 Hz,

$^2J(^{13}C\ ^{31}P)$ = 9.8 Hz, 2C, CPO_3H_2], 136.2 [*t*, $J(^{13}C\ ^{31}P)$ = 11.3 Hz, 2C, $C_{3,6}$], 116.1 (2C, C≡N), 115.5 [*t*, $J(^{13}C\ ^{31}P)$ = 5.3 Hz, 2C, $C_{1,2}$].

After the addition of base, ^{1}H NMR (300.13 MHz): δ 8.52 (*dd*, 2H), 7.34 (*br s*, NH_4^+), 4.75 (*br s*, POH and H_2O). ^{31}P NMR (121.49 MHz): δ 10.00 9.61 (*m*, 2P). ^{13}C NMR (75.47 MHz): δ 168.5 (2C, C═O), 141.3 [*dd*, $^1J(^{13}C\ ^{31}P)$ = 174.3 Hz, $^2J(^{13}C\ ^{31}P)$ = 10.6 Hz, 2C, CPO_3H_2], 134.6 134.3 (*m*, 4C), 124.6 (*s*, CO_2).

In methanol-d_4, ^{1}H NMR (300.13 MHz): δ 8.27 (*t*, *J* = 9.0 Hz, 2H, ArH). ^{31}P NMR (121.49 MHz): δ 10.93 (*s*, 2P). ^{13}C NMR (75.47 MHz): δ 170.2 (2C, C═O), 140.3 [*dd*, $^1J(^{13}C\ ^{31}P)$ = 171.7 Hz, $^2J(^{13}C\ ^{31}P)$ = 10.9 Hz, 2C, CPO_3H_2], 135.1 [*t*, $J(^{13}C\ ^{31}P)$ = 9.0 Hz, 2C, $C_{3,6}$], 133.9 [*t*, $J(^{13}C\ ^{31}P)$ = 12.1 Hz, 2C, $C_{1,2}$].

After the addition of ammonia, ^{1}H NMR (300.13 MHz): δ 8.38 (*t*, *J* = 9.0 Hz, 2H, ArH), 7.41 (*t*, *J* = 52.5 Hz, NH_4^+). ^{31}P NMR (121.49 MHz): δ 10.64 (*s*, 2P). ^{13}C NMR (75.47 MHz): δ 170.4 (2C, C═O), 141.1 [*dd*, $^1J(^{13}C\ ^{31}P)$ = 180.4 Hz, $^2J(^{13}C\ ^{31}P)$ = 10.6 Hz, 2C, CPO_3H_2], 134.9 [*t*, $J(^{13}C\ ^{31}P)$ = 4.9 Hz, 2C, $C_{3,6}$], 133.7 [*t*, $J(^{13}C\ ^{31}P)$ = 11.3 Hz, 2C, $C_{1,2}$].

2.4. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms bound to C or O atoms were placed at idealized positions, with C H = 0.95 Å (aromatic) or O H = 0.84 Å (hydroxy), and included in the final structural model in a riding-motion approximation, with the isotropic displacement parameters fixed at $1.2U_{eq}$(C) or $1.5U_{eq}$(O) of the attached atom. H atoms associated with water molecules O1*W* to O5*W* were located directly from difference Fourier maps and were included in the final structural model, with the O H and H···H distances restrained to 0.95 (1) and 1.55 (1) Å, respectively, in order to ensure a chemically reasonable environment for these groups. These H atoms were modelled with the isotropic displacement parameters fixed at $1.5U_{eq}$(O). The extra disordered water molecule was included in the final structural model distributed over three distinct crystallographic positions. Even though the H atoms associated with these partially occupied water molecules could not be located from difference Fourier maps and no attempts were made to place them in calculated positions, they have been added to the empirical formula of the compound. These moieties were included in the model by assuming a common isotropic displacement parameter.

3. Results and discussion

3.1. Synthesis and structural characterization of the organic linker: a detailed NMR study

The ^{1}H NMR spectrum of the as-prepared H_4cpp (see *Experimental*) in DMSO-d_6 shows a doublet of doublets at δ 8.05 ppm (*J* = 9.0 and 8.0 Hz) corresponding to the two phenyl-ring protons. We have, remarkably, observed a prominent triplet signal at δ 7.13 ppm (*J* = 50.6 Hz) which we have attributed ultimately to the signals of ammonium cations (Fig. S1 in the *Supporting information*). We believe that during the hydrolysis process under acidic conditions, which is detailed in the *Experimental* section, a portion of the cyano groups were decomposed and stabilized as ammonium cations. Indeed, integration of the ^{1}H NMR spectrum reveals the presence of NH_4^+ cations at about a 1:1 ratio in the final product. To date, we have been unable to crystallize this com pound in order observe unequivocally this structural feature. To validate this assumption, we have instead carried out two different sets of detailed NMR experiments in DMSO-d_6 and methanol-d_4 which are detailed in Cases 1 and 2 below.

The ^{13}C NMR studies show a peak at δ 116.1 ppm corresponding to the resonance of the two cyano groups, and a doublet of doublets at δ 114.8 ppm, with *J* of 161.6 and 9.8 Hz, correlated to the resonance of the C atoms belonging to the phosphonic acid groups. The spectrum shows two triplets at δ 136.2 and 115.5 ppm corresponding to the $C_{3,6}$ and $C_{1,2}$ carbons of the aromatic ring, respectively (Fig. S3 in the *Supporting information*).

The ^{31}P NMR spectrum shows only one signal as a multiplet between 9.38 and 9.77 ppm (Fig. S2 in the *Supporting information*).

3.1.1. Case 1: NMR studies before and after the addition of a base to the NMR tube (in DMSO-d_6). We assumed that adding an excess of base, in this case solid K_2CO_3, to the NMR tube containing H_4cpp in DMSO-d_6 would neutralize, if not all

Table 2
Selected geometric parameters (Å, °).

Ca1	O1	2.294 (3)	Ca2	O4	2.304 (3)
Ca1	O4	2.496 (3)	Ca2	O5^{i}	2.306 (3)
Ca1	O5	2.685 (3)	Ca2	O7^{i}	2.469 (3)
Ca1	O7	2.362 (3)	Ca2	O9^{i}	2.660 (3)
Ca1	O9^{i}	2.319 (3)	Ca2	O11^{i}	2.416 (3)
Ca1	O10	2.310 (3)	Ca2	N1^{ii}	2.651 (4)
Ca1	O1*W*	2.365 (3)	Ca2	O2*W*	2.459 (4)
Ca2	O2	2.546 (3)			

O1	Ca1	O4	78.35 (11)	O4	Ca2	O7^{i}	124.54 (11)
O1	Ca1	O5	77.14 (11)	O4	Ca2	O9^{i}	68.47 (10)
O1	Ca1	O7	92.53 (11)	O4	Ca2	O11^{i}	102.96 (11)
O1	Ca1	O9^{i}	98.80 (11)	O4	Ca2	N1^{ii}	87.27 (12)
O1	Ca1	O10	159.06 (12)	O4	Ca2	O2*W*	77.21 (12)
O1	Ca1	O1*W*	90.25 (13)	O5^{i}	Ca2	O2	106.02 (11)
O4	Ca1	O5	56.78 (9)	O5^{i}	Ca2	O7^{i}	74.96 (11)
O7	Ca1	O4	126.80 (11)	O5^{i}	Ca2	O9^{i}	132.30 (11)
O7	Ca1	O5	70.05 (10)	O5^{i}	Ca2	O11^{i}	89.23 (11)
O7	Ca1	O1*W*	82.00 (12)	O5^{i}	Ca2	N1^{ii}	73.48 (12)
O9^{i}	Ca1	O4	71.26 (11)	O5^{i}	Ca2	O2*W*	88.64 (12)
O9^{i}	Ca1	O5	127.75 (11)	O7^{i}	Ca2	O2	78.71 (10)
O9^{i}	Ca1	O7	160.64 (12)	O7^{i}	Ca2	O9^{i}	58.29 (10)
O9^{i}	Ca1	O1*W*	82.29 (12)	O7^{i}	Ca2	N1^{ii}	126.21 (12)
O10	Ca1	O4	89.32 (11)	O11^{i}	Ca2	O2	144.08 (11)
O10	Ca1	O5	81.95 (11)	O11^{i}	Ca2	O7^{i}	74.13 (10)
O10	Ca1	O7	81.29 (10)	O11^{i}	Ca2	O9^{i}	70.54 (10)
O10	Ca1	O9^{i}	93.05 (11)	O11^{i}	Ca2	N1^{ii}	146.04 (12)
O10	Ca1	O1*W*	108.50 (13)	O11^{i}	Ca2	O2*W*	79.17 (11)
O1*W*	Ca1	O4	148.95 (12)	O2*W*	Ca2	O2	132.19 (11)
O1*W*	Ca1	O5	148.50 (11)	O2*W*	Ca2	O7^{i}	148.61 (11)
O2	Ca2	O9^{i}	75.34 (10)	O2*W*	Ca2	O9^{i}	126.56 (11)
O2	Ca2	N1^{ii}	69.80 (12)	O2*W*	Ca2	N1^{ii}	71.58 (13)
O4	Ca2	O2	73.89 (10)	N1^{ii}	Ca2	O9^{i}	141.94 (11)
O4	Ca2	O5^{i}	159.04 (12)				

Symmetry codes: (i) x, y, z 1; (ii) x, $y+\frac{3}{2}, z$ $\frac{1}{2}$.

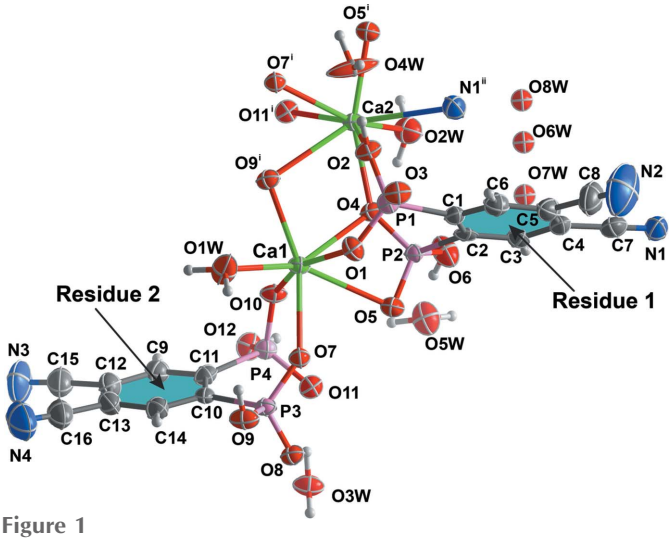


Figure 1
Schematic representation of the asymmetric unit of $\{[Ca_2(H_2cpp)_2(H_2O)_2]\ 4H_2O\}_n$, (1), showing all non H atoms as displacement ellipsoids drawn at the 50% probability level and H atoms as small spheres with an arbitrary radius. The coordination spheres of the crystallographically independent metallic centres are completed by generating the remaining O and N atoms through symmetry. For selected bond lengths (in Å) and angles (in °), see Table 2. [Symmetry codes: (i) x, y, z 1; (ii) x, $y + \frac{3}{2}$, z $\frac{1}{2}$.]

then at least in part, the ammonium cations. The ^{1}H NMR spectrum clearly shows that the triplet signal disappears. However, a new broad signal still appears in the same region, at δ 7.34 ppm (Fig. S4 in the *Supporting information*). This signal may be related to the pendant ammonium cations. At δ 4.75 ppm, we have a second broad signal correlated to the H_2O and the OH groups of phosphonic acid. Interestingly, the ^{13}C NMR spectrum shows the appearance of new signal at δ 168.5 ppm corresponding to carbonyl groups (C═O), along with the disappearance of the cyano signal at δ 124.6 ppm (Fig. S6 in the *Supporting information*). This fact seems to indicate that the addition of a base to H_4cpp ultimately converts *in situ* the cyano groups into carboxylic acid groups, forming CO_2 from carbonate.

3.1.2. Case 2: NMR studies before and after the addition of ammonia in methanol-d_4. The ^{1}H NMR spectrum of H_4cpp in methanol-d_4 shows a pseudo-triplet signal at δ 8.27 ppm corresponding to the phenyl-ring protons (Fig. S7 in the *Supporting information*). We have not observed any significant signals related to the ammonium cation. The ^{13}C NMR spectrum shows a signal at δ 170.2 ppm, which must correspond to carbonyl groups (C═O), along with the other signals (Fig. S10 in the *Supporting information*). This study reveals that, in methanol-d_4, H_4cpp undergoes an *in situ* conversion to a carboxylic acid derivative, similar to that described above, because no OCD_3 group signals, typical of an esterification, are present in the aliphatic region.

A few drops of a methanolic ammonia solution (*ca* 7 *M*) were added to the NMR tube and the ^{1}H NMR spectrum was collected again. The results show the appearance of the corresponding triplet signal of the ammonium cation at δ 7.41 ppm (J = 52.5 Hz) alongside the phenyl protons at δ 8.38 (Fig. S10 in the *Supporting information*).

Based on the aforementioned experimental data, we have confirmed that triplet signals at δ 7.13 ppm in DMSO-d_6 indeed correspond to ammonium cations. These seem to exist in the final product, probably stabilizing the organic linker as an ammonium salt.

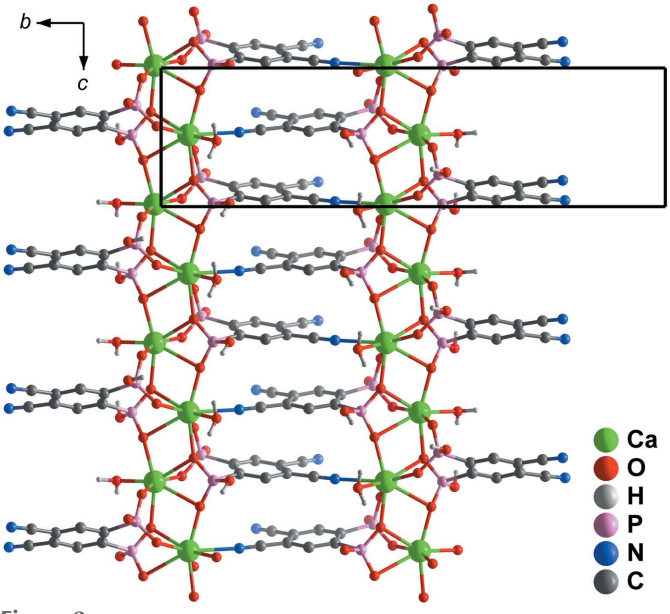


Figure 2
A one dimensional ladder like $^1_\infty[Ca_2(H_2cpp)_2(H_2O)_2]$ chain running parallel to the c axis of the unit cell. The figure emphasizes the presence of inorganic chains of Ca^{2+} cations disposed parallel to the [001] direction [Ca Ca distance of 3.9334 (12) Å] connected by organic residues. Crystallization water molecules have been removed for the sake of clarity.

3.2. Structural description of the one-dimensional ladder coordination polymer

$\{[Ca_2(H_2cpp)_2(H_2O)_2]\cdot 4H_2O\}_n$, (1) (see Scheme), crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit is composed of two metal centres (Ca1 and Ca2), two H_2cpp^{2-} residues (denoted Residues 1 and 2; Fig. 1) and four water molecules of crystallization.

Remarkably, the two metal centres do not exhibit the same coordination environment. Ca1 is heptacoordinated to one water molecule and six hydrogenophosphonate moieties, *i.e.* $\{CaO_7\}$, with the overall coordination geometry resembling a distorted pentagonal bipyramid. The Ca O bond lengths are in the range 2.294 (3) 2.685 (3) Å (see Table 2). Atom Ca2 is octacoordinated to one water molecule, six hydrogenophosphonate residues and one cyano group, *i.e.* $\{CaNO_7\}$, and the coordination environment may be described as a highly distorted square antiprism. For this metal atom, the Ca (N,O)bond lengths are in the range 2.304 (3) 2.660 (3) Å. We note that the distances for both coordination environments are well within the expected ranges, as revealed by a search in the CSD (median value of 2.38 Å for a wide range of 2.08 2.85 Å).

The two crystallographically independent H_2cpp^{2-} ligands (Residues 1 and 2; Fig. 1) act as linkers connecting three Ca^{2+}

Table 3
Hydrogen bond geometry (Å, °).

D H···*A*	*D* H	H···*A*	*D*···*A*	*D* H···*A*
O1*W* H1*X*···O3^{iii}	0.95	1.76	2.693 (4)	169
O1*W* H1*Y*···N4^{iv}	0.95	2.06	3.004 (6)	178
O2*W* H2*X*···O5*W*^{i}	0.95	1.79	2.725 (5)	167
O2*W* H2*Y*···O12^{v}	0.95	2.16	2.988 (5)	146
O3*W* H3*X*···O11	0.95	1.76	2.696 (4)	171
O3*W* H3*Y*···O10^{vi}	0.95	1.77	2.691 (4)	166
O4*W* H4*X*···O1^{i}	0.95	1.82	2.747 (5)	167
O4*W* H4*Y*···O8^{iii}	0.95	2.04	2.785 (5)	135
O5*W* H5*X*···O3*W*^{vii}	0.95	1.79	2.729 (5)	171
O5*W* H5*Y*···N3^{viii}	0.95	1.93	2.860 (6)	166
O2 H2···O4*W*	0.95	1.56	2.499 (5)	171
O6 H6···O5*W*	0.84	1.79	2.600 (5)	162
O8 H8···O3^{iii}	0.84	1.69	2.513 (4)	165
O12 H12···O3*W*^{vii}	0.84	1.76	2.596 (5)	171

Symmetry codes: (i) x, y, z 1; (iii) x, $y+1$, $z+1$; (iv) x, $y+\frac{1}{2}, z$ $\frac{1}{2}$; (v) $x+1$, $y+1$, $z+1$; (vi) $x, y, z+1$; (vii) $x+1$, $y+1$, $z+2$; (viii) $x+1$, $y+\frac{1}{2}$, $z+\frac{3}{2}$.

metallic centres. The connecting modes are, nevertheless, strikingly distinct. While Residue 1 is bound to two Ca^{2+} centres *via* the phosphonate groups and to a third metal atom using the pendant cyano group C7≡N1, Residue 2 only establishes connections *via* phosphonate groups, leaving both cyano groups unimpeded for hydrogen-bonding interactions (see Table 3). Intermetallic bridges promote the formation of a compact one-dimensional zigzag ribbon of Ca^{2+} centres running parallel to the [001] direction of the unit cell (Fig. 2), which are characterized by two distinct intermetallic distances: Ca1···Ca2 = 3.9753 (12) Å and Ca1^{i}···Ca2 = 3.9334 (12) Å [symmetry code: (i) $x, y, z+1$].

The aforementioned single connection *via* the cyano group constitutes the ultimate structural feature differentiating the two anionic H_2cpp^{2-} ligands. While Residue 1 is bound to one metal centre *via* a Ca N distance of 2.651 (4) Å (from the CSD: mean value for Ca N of 2.55 Å, with a total range of 2.21 3.21 Å), Residue 2 has both cyano groups uncoordinated. This bridge is at the genesis of a ladder-like $^{1}_{\infty}[Ca_2(H_2cpp)_2(H_2O)_2]$ chain running parallel to the [001] direction of the unit cell, as depicted in Fig. 2.

3.3. Supramolecular features

The crystal structure of compound (1) is based mostly on how the individual $^{1}_{\infty}[Ca_2(H_2cpp)_2(H_2O)_2]$ ladders close pack and interact. The various water molecules fill the voids. In the *bc* plane of the unit cell, ladders interdigitate *via* the Residue 2 organic linkers, which have both cyano groups uncoordinated. These groups are engaged in strong and highly directional O H···N hydrogen-bonding interactions with water molecules (both coordinated and of crystallization): *D*···*A* (donor acceptor) distances = 2.860 (6) 3.004 (6) Å and *D* H···*A* interaction angles = 166 178°. The immediate effect is the formation of supramolecular undulated layers located in the *bc* plane (Fig. 3, top), which alternate along the [100] direction of the unit cell. It is worthy of note that the individual

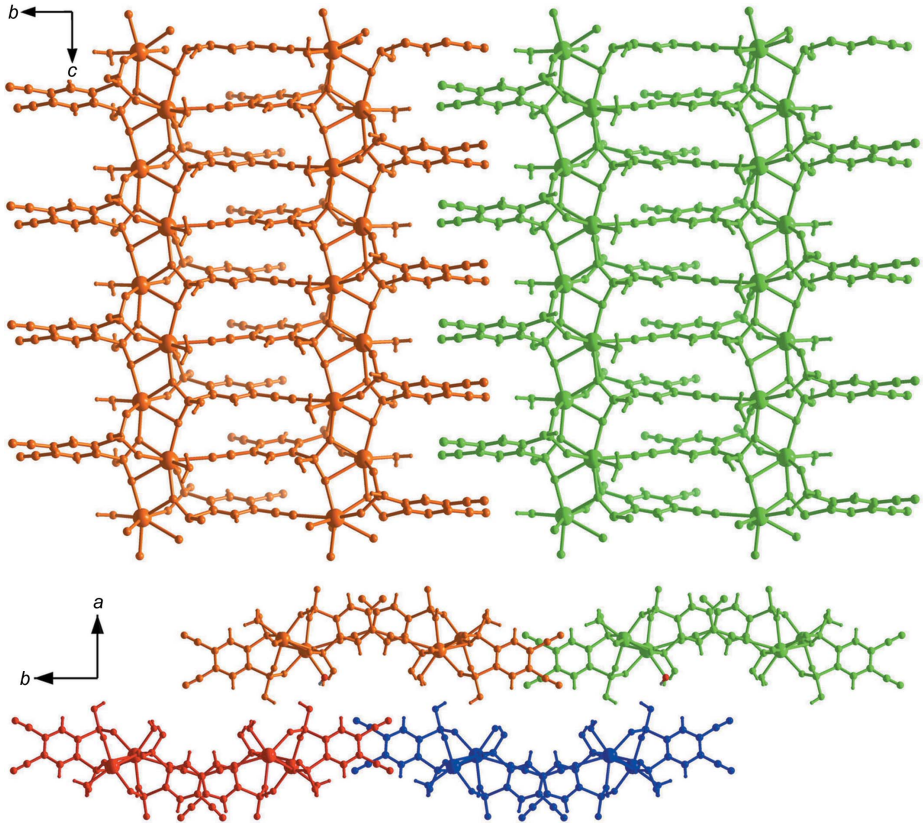


Figure 3
Schematic representation of the parallel packing of individual ladder like $^{1}_{\infty}[Ca_2(H_2cpp)_2(H_2O)_2]$ chains, viewed along the (top) [100] and (bottom) [001] directions of the unit cell. Individual ladders are represented in different colours for clarity.

$^{1}_{\infty}[Ca_2(H_2cpp)_2(H_2O)_2]$ ladders are distributed in a typical brick-wall-like fashion in the *ab* plane of the unit cell, as depicted in Fig. 3 (top).

The overall structural cohesion is significantly boosted by the presence of various additional O H···O and O H···N hydrogen-bond interactions. Water molecules and hydroxy groups promote a network of strong connections, with *D*···*A* distances ranging from as low as 2.499 (5) to 2.988 (5) Å; the corresponding *D* H···*A* interaction angles are found in the 135 171° range (Table 3). These contacts lead to a network of connections between all groups, as depicted in Fig. 4.

4. Conclusions

We have reported the synthesis and detailed structural characterization of the novel organic linker (4,5-dicyano-1,2-phenylene)bis(phosphonic acid) (H_4cpp) and its use in the self-assembly of a one-dimensional ladder-like $^{1}_{\infty}[Ca_2(H_2cpp)_2(H_2O)_2]$ chain isolated in the crystalline compound $\{[Ca_2(H_2cpp)_2(H_2O)_2]\cdot 4H_2O\}_n$. To the best of our knowledge, the compound is a rare example of a Ca^{2+}-based CP based on a cyanophosphonate or an aminophosphonate linker. We are currently exploring in our laboratories the use of this organic linker to prepare other polymeric structures using other *s*-block cations.

Acknowledgements

Funding sources and bodies: Fundação para a Ciência e a Tecnologia (FCT, Portugal), the European Union, QREN, FEDER through Programa Operacional Factores de Competitividade (COMPETE), CICECO Aveiro Institute of Mate-

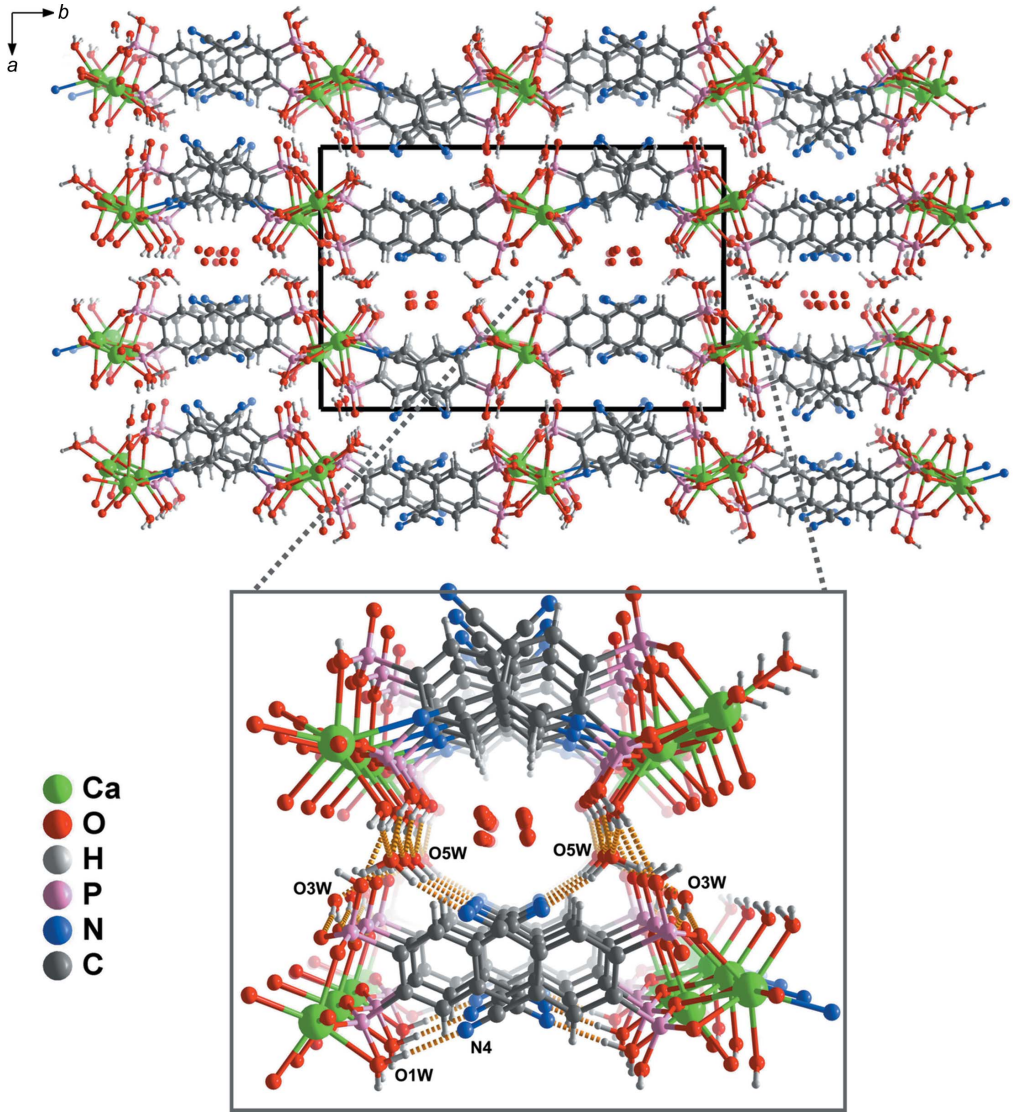


Figure 4
The crystal packing of $\{[Ca_2(H_2cpp)_2(H_2O)_2]\ 4H_2O\}_n$, (1), viewed in perspective along the [001] direction of the unit cell. The magnification focuses on the strong and directional O H O and O H N hydrogen bonding interactions (orange dashed lines) connecting together water molecules and adjacent $^{1}_{\infty}[Ca_2(H_2cpp)_2(H_2O)_2]$ chains (*via* the uncoordinated hydroxy and cyano groups). For geometrical details of the represented hydrogen bonding interactions, see Table 3. Symmetry transformations used to generate equivalent atoms have been omitted for clarity.

rials (reference FCT UID/CTM/50011/2013), QOPNA (reference FCT UID/QUI/00062/2013) and CQE (reference FCT UID/QUI/0100/2013) research units, financed by national funds through the FCT/MEC and when applicable co-financed by FEDER under the PT2020 Partnership Agreement.

Projects and individual grants: We wish to thank FCT for funding the R&D project FCOMP-01-0124-FEDER-041282 (reference FCT EXPL/CTM-NAN/0013/2013), and also CICECO for specific funding towards the purchase of the single-crystal diffractometer. FCT is gratefully acknowledged for postdoctoral research grant No. SFRH/BPD/79000/2011 (to NV) and PhD research grant No. SFRH/BD/84231/2012 (to RFM).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380 388.
Bishop, M., Bott, S. G. & Barron, A. R. (2003). *Chem. Mater.* **15**, 3074 3088.
Brandenburg, K. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2012). *SAINT* and *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Demadis, K. D., Barouda, E., Stavgianoudaki, N. & Zhao, H. (2009). *Cryst. Growth Des.* **9**, 1250 1253.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171 179.
Liang, X., Zhang, F., Feng, W., Zou, X., Zhao, C., Na, H., Liu, C., Sun, F. & Zhu, G. (2013). *J. Chem. Sci.* **4**, 983 992.
Mendes, R. F., Silva, P., Antunes, M. M., Valente, A. A. & Paz, F. A. A. (2015). *Chem. Commun.* **51**, 10807 10810.
Schmidt, C., Feyand, M., Rothkirch, A. & Stock, N. (2011). *J. Solid State Chem.* **188**, 44 49.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3 8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3 8.
Stock, N. & Bein, T. (2004). *Angew. Chem. Int. Ed.* **43**, 749 752.
Venkatramaiah, N., Pereira, P. M. R., Paz, F. A. A., Ribeiro, C. A. F., Fernandes, R. & Tomé, J. P. C. (2015). *Chem. Commun.* **51**, 15550 15553.
Yang, X. L., Hou, G. H., Guan, R. F., Shao, R. & Xie, M. H. (2016). *Adv. Funct. Mater.* **26**, 393 398.
Zhai, Q. G., Bu, X., Mao, C., Zhao, X. & Feng, P. (2016). *J. Am. Chem. Soc.* **138**, 2524 2527.

supporting information

Acta Cryst. (2016). C**72**, 685-691 [doi:10.1107/S2053229616012328]

A ladder coordination polymer based on Ca^{2+} and (4,5-dicyano-1,2-phenylene)bis(phosphonic acid): crystal structure and solution-state NMR study

Nutalapati Venkatramaiah, Ricardo F. Mendes, Artur M. S. Silva, João P. C. Tomé and Filipe A. Almeida Paz

Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b).

Poly[[diaqua[μ_4-(4,5-dicyano-1,2-phenylene)bis(phosphonato)][μ_3-(4,5-dicyano-1,2-phenylene)bis(phosphonato)]dicalcium(II)] tetrahydrate]

Crystal data

$[Ca_2(C_8H_4N_2O_6P_2)_2(H_2O)_2]\cdot 4H_2O$
M_r = 760.40
Monoclinic, $P2_1/c$
a = 16.4384 (11) Å
b = 25.2929 (18) Å
c = 6.9599 (5) Å
β = 91.493 (3)°
V = 2892.8 (4) Å^3
Z = 4
$F(000)$ = 1552
D_x = 1.746 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9894 reflections
θ = 2.5–27.5°
μ = 0.70 mm^{-1}
T = 180 K
Needle, colourless
0.10 × 0.06 × 0.01 mm

Data collection

Bruker D8 QUEST diffractometer
Radiation source: Sealed tube
Multi-layer X-ray mirror monochromator
Detector resolution: 10.4167 pixels mm^{-1}
ω / φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2001)
T_{min} = 0.665, T_{max} = 0.746
27705 measured reflections
5266 independent reflections
4050 reflections with $I > 2\sigma(I)$
R_{int} = 0.065
θ_{max} = 25.3°, θ_{min} = 3.6°
h = −19→19
k = −30→30
l = −8→6

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.133
S = 1.12
5266 reflections
437 parameters
17 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0456P)^2 + 10.5068P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 1.11$ e Å ^{3}
$\Delta\rho_{min} = -0.46$ e Å ^{3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ca1	0.21357 (5)	0.48752 (4)	0.48298 (12)	0.0121 (2)	
O1W	0.1289 (2)	0.41194 (14)	0.4757 (5)	0.0283 (9)	
H1X	0.083 (2)	0.4128 (18)	0.556 (7)	0.042*	
H1Y	0.149 (3)	0.3768 (8)	0.467 (8)	0.042*	
Ca2	0.26293 (5)	0.55449 (4)	−0.01741 (12)	0.0129 (2)	
O2W	0.3849 (2)	0.60987 (14)	0.0272 (5)	0.0251 (8)	
H2X	0.416 (3)	0.605 (2)	−0.084 (4)	0.038*	
H2Y	0.414 (3)	0.597 (2)	0.137 (4)	0.038*	
P1	0.07803 (7)	0.57959 (5)	0.28875 (17)	0.0137 (3)	
P2	0.27497 (7)	0.60345 (5)	0.47447 (16)	0.0123 (3)	
P3	0.19620 (7)	0.44154 (5)	0.98306 (16)	0.0127 (3)	
P4	0.38005 (7)	0.44944 (5)	0.76973 (16)	0.0133 (3)	
O1	0.10166 (18)	0.54102 (12)	0.4433 (4)	0.0163 (7)	
O2	0.11751 (18)	0.56490 (13)	0.0942 (4)	0.0159 (7)	
H2	0.081 (2)	0.560 (2)	−0.012 (5)	0.024*	
O3	−0.01218 (18)	0.58811 (13)	0.2597 (4)	0.0177 (7)	
O4	0.27202 (18)	0.56479 (12)	0.3114 (4)	0.0156 (7)	
O5	0.26030 (19)	0.57702 (13)	0.6615 (4)	0.0183 (7)	
O6	0.35591 (19)	0.63571 (13)	0.4760 (5)	0.0236 (8)	
H6	0.3892	0.6223	0.5558	0.035*	
O7	0.19488 (18)	0.47961 (12)	0.8170 (4)	0.0137 (7)	
O8	0.11072 (19)	0.41838 (13)	1.0214 (4)	0.0185 (7)	
H8	0.0848	0.4147	0.9166	0.028*	
O9	0.23133 (18)	0.46456 (12)	1.1642 (4)	0.0153 (7)	
O10	0.34371 (18)	0.46164 (13)	0.5742 (4)	0.0161 (7)	
O11	0.36883 (18)	0.49098 (12)	0.9206 (4)	0.0150 (7)	
O12	0.47252 (18)	0.43474 (13)	0.7524 (5)	0.0195 (7)	
H12	0.4995	0.4622	0.7312	0.029*	
N1	0.2182 (3)	0.84492 (17)	0.4633 (6)	0.0232 (9)	
N2	−0.0175 (4)	0.8114 (2)	0.3213 (10)	0.0628 (18)	
N3	0.4199 (3)	0.2033 (2)	0.8105 (8)	0.0445 (13)	
N4	0.1946 (4)	0.1987 (2)	0.9551 (8)	0.0480 (14)	
C1	0.1198 (3)	0.64455 (18)	0.3556 (6)	0.0145 (9)	
C2	0.1994 (3)	0.65507 (18)	0.4251 (6)	0.0141 (9)	
C3	0.2237 (3)	0.70717 (18)	0.4555 (6)	0.0174 (10)	
H3	0.2778	0.7144	0.4992	0.021*	

C4	0.1697 (3)	0.74911 (19)	0.4227 (6)	0.0199 (10)	
C5	0.0894 (3)	0.73801 (19)	0.3647 (7)	0.0209 (11)	
C6	0.0661 (3)	0.68640 (19)	0.3304 (7)	0.0192 (10)	
H6A	0.0118	0.6793	0.2884	0.023*	
C7	0.1968 (3)	0.8027 (2)	0.4459 (7)	0.0243 (11)	
C8	0.0308 (4)	0.7803 (2)	0.3392 (8)	0.0324 (13)	
C9	0.3783 (3)	0.34030 (19)	0.8153 (7)	0.0198 (10)	
H9	0.4320	0.3420	0.7684	0.024*	
C10	0.2573 (3)	0.38361 (18)	0.9209 (6)	0.0132 (9)	
C11	0.3358 (3)	0.38678 (18)	0.8459 (6)	0.0156 (10)	
C12	0.3442 (3)	0.2914 (2)	0.8519 (7)	0.0225 (11)	
C13	0.2651 (3)	0.28838 (19)	0.9180 (7)	0.0221 (11)	
C14	0.2224 (3)	0.33432 (19)	0.9546 (7)	0.0191 (10)	
H14	0.1690	0.3323	1.0030	0.023*	
C15	0.3892 (3)	0.2431 (2)	0.8245 (8)	0.0297 (12)	
C16	0.2254 (3)	0.2379 (2)	0.9432 (8)	0.0275 (12)	
O3W	0.43889 (19)	0.48070 (14)	1.2731 (5)	0.0200 (7)	
H3X	0.411 (2)	0.481 (2)	1.152 (3)	0.030*	
H3Y	0.401 (2)	0.479 (2)	1.373 (4)	0.030*	
O4W	0.0320 (3)	0.5554 (3)	−0.2061 (6)	0.073 (2)	
H4X	0.051 (4)	0.546 (4)	−0.328 (5)	0.109*	
H4Y	−0.0246 (12)	0.562 (4)	−0.213 (10)	0.109*	
O5W	0.4773 (2)	0.61236 (15)	0.7077 (5)	0.0267 (8)	
H5X	0.502 (3)	0.5783 (8)	0.711 (9)	0.040*	
H5Y	0.519 (2)	0.6385 (12)	0.706 (8)	0.040*	
O6W	0.4021 (8)	0.7237 (5)	0.106 (2)	0.055 (2)*	0.375 (8)
O7W	0.4377 (11)	0.7206 (7)	0.296 (3)	0.055 (2)*	0.262 (8)
O8W	0.3948 (8)	0.7254 (5)	−0.046 (2)	0.055 (2)*	0.363 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0123 (4)	0.0148 (5)	0.0091 (4)	0.0004 (4)	0.0009 (3)	0.0008 (4)
O1W	0.034 (2)	0.022 (2)	0.030 (2)	−0.0097 (16)	0.0191 (16)	−0.0055 (16)
Ca2	0.0161 (5)	0.0137 (5)	0.0090 (4)	0.0008 (4)	0.0002 (3)	−0.0001 (4)
O2W	0.0251 (19)	0.028 (2)	0.0225 (18)	−0.0025 (16)	−0.0002 (15)	0.0023 (16)
P1	0.0114 (6)	0.0153 (6)	0.0143 (6)	0.0002 (5)	0.0008 (4)	−0.0004 (5)
P2	0.0145 (6)	0.0125 (6)	0.0098 (5)	−0.0017 (5)	−0.0009 (4)	0.0003 (5)
P3	0.0131 (6)	0.0150 (6)	0.0100 (5)	−0.0017 (5)	0.0015 (4)	0.0006 (5)
P4	0.0120 (6)	0.0153 (6)	0.0127 (5)	0.0006 (5)	0.0007 (4)	0.0003 (5)
O1	0.0146 (16)	0.0156 (17)	0.0188 (16)	0.0004 (13)	0.0005 (13)	0.0027 (13)
O2	0.0138 (16)	0.0210 (18)	0.0129 (15)	−0.0006 (13)	−0.0001 (12)	−0.0028 (13)
O3	0.0132 (16)	0.0242 (19)	0.0158 (16)	0.0008 (14)	0.0002 (13)	−0.0004 (14)
O4	0.0192 (17)	0.0173 (17)	0.0103 (15)	0.0012 (13)	0.0013 (13)	−0.0008 (13)
O5	0.0252 (18)	0.0179 (18)	0.0120 (15)	0.0010 (14)	0.0013 (13)	0.0018 (13)
O6	0.0158 (17)	0.0222 (19)	0.032 (2)	−0.0029 (14)	−0.0074 (15)	0.0064 (16)
O7	0.0141 (16)	0.0139 (17)	0.0132 (15)	0.0000 (12)	0.0018 (12)	0.0000 (13)
O8	0.0144 (16)	0.0270 (19)	0.0141 (16)	−0.0046 (14)	0.0009 (13)	0.0006 (15)

O9	0.0160 (16)	0.0183 (17)	0.0118 (15)	−0.0017 (13)	0.0016 (12)	−0.0006 (13)
O10	0.0144 (16)	0.0226 (18)	0.0115 (15)	0.0009 (13)	0.0028 (12)	0.0010 (13)
O11	0.0119 (15)	0.0172 (17)	0.0158 (16)	0.0006 (13)	0.0005 (12)	−0.0012 (13)
O12	0.0135 (16)	0.0217 (19)	0.0235 (18)	0.0022 (13)	0.0013 (14)	−0.0011 (15)
N1	0.031 (2)	0.018 (2)	0.021 (2)	−0.0016 (19)	0.0066 (18)	−0.0019 (18)
N2	0.053 (4)	0.043 (4)	0.092 (5)	0.023 (3)	−0.013 (3)	−0.016 (3)
N3	0.048 (3)	0.023 (3)	0.062 (4)	0.013 (2)	−0.002 (3)	−0.005 (3)
N4	0.061 (4)	0.030 (3)	0.053 (3)	−0.012 (3)	−0.007 (3)	0.005 (3)
C1	0.019 (2)	0.014 (2)	0.010 (2)	−0.0018 (19)	0.0021 (18)	−0.0012 (18)
C2	0.019 (2)	0.018 (2)	0.006 (2)	−0.0012 (19)	0.0037 (17)	0.0014 (18)
C3	0.024 (3)	0.017 (2)	0.012 (2)	−0.004 (2)	0.0039 (19)	0.0016 (19)
C4	0.034 (3)	0.014 (2)	0.012 (2)	−0.002 (2)	0.004 (2)	−0.0014 (19)
C5	0.026 (3)	0.021 (3)	0.016 (2)	0.008 (2)	0.003 (2)	0.001 (2)
C6	0.019 (2)	0.021 (3)	0.017 (2)	0.001 (2)	−0.0007 (19)	0.001 (2)
C7	0.035 (3)	0.024 (3)	0.014 (2)	0.004 (2)	0.006 (2)	−0.001 (2)
C8	0.038 (3)	0.021 (3)	0.038 (3)	0.009 (3)	−0.004 (3)	−0.005 (2)
C9	0.023 (3)	0.020 (3)	0.016 (2)	0.003 (2)	−0.0018 (19)	0.000 (2)
C10	0.019 (2)	0.012 (2)	0.008 (2)	0.0015 (18)	−0.0020 (17)	0.0001 (17)
C11	0.016 (2)	0.018 (3)	0.013 (2)	0.0002 (19)	−0.0016 (18)	−0.0023 (19)
C12	0.029 (3)	0.018 (3)	0.020 (2)	0.006 (2)	−0.001 (2)	0.001 (2)
C13	0.030 (3)	0.017 (3)	0.020 (2)	−0.002 (2)	−0.003 (2)	0.003 (2)
C14	0.022 (3)	0.018 (3)	0.017 (2)	−0.003 (2)	0.0001 (19)	−0.001 (2)
C15	0.036 (3)	0.022 (3)	0.030 (3)	0.002 (2)	−0.005 (2)	−0.002 (2)
C16	0.032 (3)	0.021 (3)	0.029 (3)	−0.003 (2)	−0.005 (2)	0.001 (2)
O3W	0.0147 (17)	0.030 (2)	0.0157 (16)	0.0005 (14)	0.0019 (13)	0.0027 (15)
O4W	0.024 (2)	0.173 (6)	0.021 (2)	0.030 (3)	−0.0032 (17)	−0.023 (3)
O5W	0.0198 (19)	0.025 (2)	0.035 (2)	−0.0024 (15)	−0.0017 (16)	0.0026 (17)

Geometric parameters (Å, º)

Ca1—O1	2.294 (3)	O6—H6	0.8400
Ca1—O4	2.496 (3)	O7—Ca2^{ii}	2.470 (3)
Ca1—O5	2.685 (3)	O8—H8	0.8400
Ca1—O7	2.362 (3)	O9—Ca1^{ii}	2.319 (3)
Ca1—O9^{i}	2.319 (3)	O9—Ca2^{ii}	2.660 (3)
Ca1—O10	2.310 (3)	O11—Ca2^{ii}	2.416 (3)
Ca1—O1W	2.365 (3)	O12—H12	0.8400
Ca1—Ca2^{ii}	3.9334 (12)	N1—C7	1.130 (6)
Ca1—Ca2	3.9753 (12)	N1—Ca2^{iv}	2.651 (4)
O1W—H1X	0.947 (10)	N2—C8	1.122 (7)
O1W—H1Y	0.949 (10)	N3—C15	1.130 (7)
Ca2—O2	2.546 (3)	N4—C16	1.117 (7)
Ca2—O4	2.304 (3)	C1—C6	1.386 (7)
Ca2—O5^{i}	2.306 (3)	C1—C2	1.409 (6)
Ca2—O7^{i}	2.469 (3)	C2—C3	1.392 (6)
Ca2—O9^{i}	2.660 (3)	C3—C4	1.399 (7)
Ca2—O11^{i}	2.416 (3)	C3—H3	0.9500
Ca2—N1^{iii}	2.651 (4)	C4—C5	1.398 (7)

Ca2—O2W	2.459 (4)	C4—C7	1.434 (7)
O2W—H2X	0.948 (10)	C5—C6	1.379 (7)
O2W—H2Y	0.946 (10)	C5—C8	1.449 (7)
P1—O1	1.496 (3)	C6—H6A	0.9500
P1—O3	1.507 (3)	C9—C12	1.384 (7)
P1—O2	1.562 (3)	C9—C11	1.388 (7)
P1—C1	1.836 (5)	C9—H9	0.9500
P2—O5	1.489 (3)	C10—C14	1.395 (6)
P2—O4	1.498 (3)	C10—C11	1.406 (6)
P2—O6	1.561 (3)	C12—C13	1.392 (7)
P2—C2	1.828 (5)	C12—C15	1.445 (7)
P3—O9	1.492 (3)	C13—C14	1.385 (7)
P3—O7	1.504 (3)	C13—C16	1.448 (7)
P3—O8	1.552 (3)	C14—H14	0.9500
P3—C10	1.834 (5)	O3W—H3X	0.946 (10)
P3—Ca2^{ii}	3.0603 (15)	O3W—H3Y	0.945 (10)
P4—O11	1.500 (3)	O4W—H4X	0.946 (10)
P4—O10	1.504 (3)	O4W—H4Y	0.945 (10)
P4—O12	1.573 (3)	O5W—H5X	0.949 (10)
P4—C11	1.828 (5)	O5W—H5Y	0.949 (10)
O2—H2	0.947 (10)	O6W—O8W	1.061 (16)
O5—Ca2^{ii}	2.306 (3)	O6W—O7W	1.44 (2)

O1—Ca1—O4	78.35 (11)	O9—P3—Ca2^{ii}	60.36 (13)
O1—Ca1—O5	77.14 (11)	O7—P3—Ca2^{ii}	53.09 (12)
O1—Ca1—O7	92.53 (11)	O8—P3—Ca2^{ii}	132.75 (14)
O1—Ca1—O9^{i}	98.80 (11)	C10—P3—Ca2^{ii}	123.16 (15)
O1—Ca1—O10	159.06 (12)	O11—P4—O10	115.88 (18)
O1—Ca1—O1W	90.25 (13)	O11—P4—O12	110.84 (18)
O4—Ca1—O5	56.78 (9)	O10—P4—O12	109.95 (18)
O7—Ca1—O4	126.80 (11)	O11—P4—C11	110.31 (19)
O7—Ca1—O5	70.05 (10)	O10—P4—C11	106.76 (19)
O7—Ca1—O1W	82.00 (12)	O12—P4—C11	102.1 (2)
O9^{i}—Ca1—O4	71.26 (11)	O11—P4—Ca1	95.65 (12)
O9^{i}—Ca1—O5	127.75 (11)	O12—P4—Ca1	140.23 (13)
O9^{i}—Ca1—O7	160.64 (12)	C11—P4—Ca1	95.34 (15)
O9^{i}—Ca1—O1W	82.29 (12)	P1—O1—Ca1	131.58 (18)
O10—Ca1—O4	89.32 (11)	P1—O2—Ca2	134.73 (17)
O10—Ca1—O5	81.95 (11)	P1—O2—H2	116 (3)
O10—Ca1—O7	81.29 (10)	Ca2—O2—H2	110 (3)
O10—Ca1—O9^{i}	93.05 (11)	P2—O4—Ca2	145.71 (19)
O10—Ca1—O1W	108.50 (13)	P2—O4—Ca1	98.86 (15)
O1W—Ca1—O4	148.95 (12)	Ca2—O4—Ca1	111.77 (13)
O1W—Ca1—O5	148.50 (11)	P2—O5—Ca2^{ii}	163.6 (2)
Ca1—O1W—H1X	116 (3)	P2—O5—Ca1	91.42 (15)
Ca1—O1W—H1Y	124 (3)	Ca2^{ii}—O5—Ca1	103.77 (12)
H1X—O1W—H1Y	109.7 (16)	P2—O6—H6	109.5
O2—Ca2—O9^{i}	75.34 (10)	P3—O7—Ca1	144.20 (18)

O2—Ca2—N1^{iii}	69.80 (12)	P3—O7—Ca2^{ii}	97.78 (15)
O4—Ca2—O2	73.89 (10)	Ca1—O7—Ca2^{ii}	108.99 (12)
O4—Ca2—O5^{i}	159.04 (12)	P3—O8—H8	109.5
O4—Ca2—O7^{i}	124.54 (11)	P3—O9—Ca1^{ii}	148.31 (19)
O4—Ca2—O9^{i}	68.47 (10)	P3—O9—Ca2^{ii}	90.47 (14)
O4—Ca2—O11^{i}	102.96 (11)	Ca1^{ii}—O9—Ca2^{ii}	105.75 (12)
O4—Ca2—N1^{iii}	87.27 (12)	P4—O10—Ca1	130.54 (17)
O4—Ca2—O2W	77.21 (12)	P4—O11—Ca2^{ii}	133.87 (17)
O5^{i}—Ca2—O2	106.02 (11)	P4—O12—H12	109.5
O5^{i}—Ca2—O7^{i}	74.96 (11)	C7—N1—Ca2^{iv}	176.2 (4)
O5^{i}—Ca2—O9^{i}	132.30 (11)	C6—C1—C2	118.8 (4)
O5^{i}—Ca2—O11^{i}	89.23 (11)	C6—C1—P1	114.8 (3)
O5^{i}—Ca2—N1^{iii}	73.48 (12)	C2—C1—P1	126.4 (4)
O5^{i}—Ca2—O2W	88.64 (12)	C3—C2—C1	119.4 (4)
O7^{i}—Ca2—O2	78.71 (10)	C3—C2—P2	117.2 (3)
O7^{i}—Ca2—O9^{i}	58.29 (10)	C1—C2—P2	123.4 (4)
O7^{i}—Ca2—N1^{iii}	126.21 (12)	C2—C3—C4	121.0 (4)
O11^{i}—Ca2—O2	144.08 (11)	C2—C3—H3	119.5
O11^{i}—Ca2—O7^{i}	74.13 (10)	C4—C3—H3	119.5
O11^{i}—Ca2—O9^{i}	70.54 (10)	C5—C4—C3	119.1 (4)
O11^{i}—Ca2—N1^{iii}	146.04 (12)	C5—C4—C7	120.7 (5)
O11^{i}—Ca2—O2W	79.17 (11)	C3—C4—C7	120.2 (5)
O2W—Ca2—O2	132.19 (11)	C6—C5—C4	119.7 (4)
O2W—Ca2—O7^{i}	148.61 (11)	C6—C5—C8	119.8 (5)
O2W—Ca2—O9^{i}	126.56 (11)	C4—C5—C8	120.5 (5)
O2W—Ca2—N1^{iii}	71.58 (13)	C5—C6—C1	121.9 (4)
N1^{iii}—Ca2—O9^{i}	141.94 (11)	C5—C6—H6A	119.1
Ca2—O2W—H2X	106 (3)	C1—C6—H6A	119.1
Ca2—O2W—H2Y	107 (3)	N1—C7—C4	179.7 (6)
H2X—O2W—H2Y	109.9 (16)	N2—C8—C5	176.7 (7)
O1—P1—O3	115.22 (18)	C12—C9—C11	121.3 (5)
O1—P1—O2	111.24 (18)	C12—C9—H9	119.4
O3—P1—O2	110.33 (17)	C11—C9—H9	119.4
O1—P1—C1	108.25 (19)	C14—C10—C11	119.9 (4)
O3—P1—C1	105.4 (2)	C14—C10—P3	116.4 (3)
O2—P1—C1	105.74 (19)	C11—C10—P3	123.7 (3)
O3—P1—Ca1	140.12 (14)	C9—C11—C10	118.7 (4)
O2—P1—Ca1	84.33 (12)	C9—C11—P4	118.9 (4)
C1—P1—Ca1	105.64 (15)	C10—C11—P4	122.2 (3)
O5—P2—O4	111.50 (18)	C9—C12—C13	119.8 (5)
O5—P2—O6	112.72 (19)	C9—C12—C15	121.3 (5)
O4—P2—O6	110.94 (19)	C13—C12—C15	118.9 (5)
O5—P2—C2	111.11 (19)	C14—C13—C12	119.7 (5)
O4—P2—C2	108.38 (19)	C14—C13—C16	119.1 (5)
O6—P2—C2	101.7 (2)	C12—C13—C16	121.1 (5)
O5—P2—Ca1	59.91 (13)	C13—C14—C10	120.4 (5)
O4—P2—Ca1	52.64 (12)	C13—C14—H14	119.8
O6—P2—Ca1	140.52 (14)	C10—C14—H14	119.8

C2—P2—Ca1	117.31 (15)	N3—C15—C12	174.7 (6)
O9—P3—O7	113.39 (18)	N4—C16—C13	177.3 (6)
O9—P3—O8	109.54 (18)	H3X—O3W—H3Y	110.3 (16)
O7—P3—O8	112.27 (18)	H4X—O4W—H4Y	110.4 (17)
O9—P3—C10	107.99 (19)	H5X—O5W—H5Y	109.4 (16)
O7—P3—C10	109.11 (18)	O8W—O6W—O7W	162.5 (16)
O8—P3—C10	104.0 (2)		

O3—P1—O1—Ca1	152.6 (2)	P1—C1—C2—P2	−3.6 (6)
O2—P1—O1—Ca1	26.1 (3)	O5—P2—C2—C3	102.5 (4)
C1—P1—O1—Ca1	−89.7 (3)	O4—P2—C2—C3	−134.6 (3)
O1—P1—O2—Ca2	−60.0 (3)	O6—P2—C2—C3	−17.6 (4)
O3—P1—O2—Ca2	170.9 (2)	Ca1—P2—C2—C3	168.6 (3)
C1—P1—O2—Ca2	57.3 (3)	O5—P2—C2—C1	−78.7 (4)
Ca1—P1—O2—Ca2	−47.3 (2)	O4—P2—C2—C1	44.2 (4)
O5—P2—O4—Ca2	165.4 (3)	O6—P2—C2—C1	161.1 (4)
O6—P2—O4—Ca2	−68.1 (4)	Ca1—P2—C2—C1	−12.6 (4)
C2—P2—O4—Ca2	42.7 (4)	C1—C2—C3—C4	1.6 (6)
Ca1—P2—O4—Ca2	153.5 (4)	P2—C2—C3—C4	−179.5 (3)
O5—P2—O4—Ca1	11.8 (2)	C2—C3—C4—C5	2.1 (7)
O6—P2—O4—Ca1	138.38 (16)	C2—C3—C4—C7	−177.0 (4)
C2—P2—O4—Ca1	−110.76 (17)	C3—C4—C5—C6	−3.6 (7)
O4—P2—O5—Ca2^{ii}	147.1 (7)	C7—C4—C5—C6	175.5 (4)
O6—P2—O5—Ca2^{ii}	21.6 (8)	C3—C4—C5—C8	176.8 (5)
C2—P2—O5—Ca2^{ii}	−91.9 (7)	C7—C4—C5—C8	−4.1 (7)
Ca1—P2—O5—Ca2^{ii}	158.0 (8)	C4—C5—C6—C1	1.3 (7)
O4—P2—O5—Ca1	−10.87 (19)	C8—C5—C6—C1	−179.0 (5)
O6—P2—O5—Ca1	−136.43 (16)	C2—C1—C6—C5	2.5 (7)
C2—P2—O5—Ca1	110.16 (18)	P1—C1—C6—C5	−176.6 (4)
O9—P3—O7—Ca1	141.4 (3)	O9—P3—C10—C14	105.1 (4)
O8—P3—O7—Ca1	−93.8 (3)	O7—P3—C10—C14	−131.3 (3)
C10—P3—O7—Ca1	21.0 (4)	O8—P3—C10—C14	−11.3 (4)
Ca2^{ii}—P3—O7—Ca1	138.7 (3)	Ca2^{ii}—P3—C10—C14	170.9 (3)
O9—P3—O7—Ca2^{ii}	2.8 (2)	O9—P3—C10—C11	−74.0 (4)
O8—P3—O7—Ca2^{ii}	127.57 (16)	O7—P3—C10—C11	49.7 (4)
C10—P3—O7—Ca2^{ii}	−117.63 (17)	O8—P3—C10—C11	169.7 (4)
O7—P3—O9—Ca1^{ii}	119.5 (4)	Ca2^{ii}—P3—C10—C11	−8.1 (4)
O8—P3—O9—Ca1^{ii}	−6.8 (4)	C12—C9—C11—C10	1.9 (7)
C10—P3—O9—Ca1^{ii}	−119.5 (4)	C12—C9—C11—P4	−173.3 (4)
Ca2^{ii}—P3—O9—Ca1^{ii}	122.0 (4)	C14—C10—C11—C9	−3.0 (6)
O7—P3—O9—Ca2^{ii}	−2.54 (18)	P3—C10—C11—C9	176.1 (3)
O8—P3—O9—Ca2^{ii}	−128.81 (16)	C14—C10—C11—P4	172.1 (3)
C10—P3—O9—Ca2^{ii}	118.48 (17)	P3—C10—C11—P4	−8.9 (5)
O11—P4—O10—Ca1	−52.1 (3)	O11—P4—C11—C9	−137.4 (4)
O12—P4—O10—Ca1	−178.8 (2)	O10—P4—C11—C9	95.9 (4)
C11—P4—O10—Ca1	71.2 (3)	O12—P4—C11—C9	−19.6 (4)
O10—P4—O11—Ca2^{ii}	32.3 (3)	Ca1—P4—C11—C9	124.5 (4)
O12—P4—O11—Ca2^{ii}	158.5 (2)	O11—P4—C11—C10	47.5 (4)

C11—P4—O11—Ca2^{ii}	−89.1 (3)	O10—P4—C11—C10	−79.2 (4)
Ca1—P4—O11—Ca2^{ii}	8.7 (2)	O12—P4—C11—C10	165.4 (4)
O1—P1—C1—C6	−135.0 (3)	Ca1—P4—C11—C10	−50.5 (4)
O3—P1—C1—C6	−11.2 (4)	C11—C9—C12—C13	0.9 (7)
O2—P1—C1—C6	105.7 (3)	C11—C9—C12—C15	−178.5 (5)
Ca1—P1—C1—C6	−165.9 (3)	C9—C12—C13—C14	−2.8 (7)
O1—P1—C1—C2	45.9 (4)	C15—C12—C13—C14	176.7 (5)
O3—P1—C1—C2	169.7 (4)	C9—C12—C13—C16	175.1 (5)
O2—P1—C1—C2	−73.4 (4)	C15—C12—C13—C16	−5.5 (7)
Ca1—P1—C1—C2	15.0 (4)	C12—C13—C14—C10	1.7 (7)
C6—C1—C2—C3	−3.9 (6)	C16—C13—C14—C10	−176.2 (4)
P1—C1—C2—C3	175.1 (3)	C11—C10—C14—C13	1.2 (7)
C6—C1—C2—P2	177.3 (3)	P3—C10—C14—C13	−177.9 (4)

Symmetry codes: (i) *x*, *y*, *z*−1; (ii) *x*, *y*, *z*+1; (iii) *x*, −*y*+3/2, *z*−1/2; (iv) *x*, −*y*+3/2, *z*+1/2.

Hydrogen bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*X*···O3^{v}	0.95	1.76	2.693 (4)	169
O1*W*—H1*Y*···N4^{vi}	0.95	2.06	3.004 (6)	178
O2*W*—H2*X*···O5*W*^{i}	0.95	1.79	2.725 (5)	167
O2*W*—H2*Y*···O12^{vii}	0.95	2.16	2.988 (5)	146
O3*W*—H3*X*···O11	0.95	1.76	2.696 (4)	171
O3*W*—H3*Y*···O10^{ii}	0.95	1.77	2.691 (4)	166
O4*W*—H4*X*···O1^{i}	0.95	1.82	2.747 (5)	167
O4*W*—H4*Y*···O8^{v}	0.95	2.04	2.785 (5)	135
O5*W*—H5*X*···O3*W*^{viii}	0.95	1.79	2.729 (5)	171
O5*W*—H5*Y*···N3^{ix}	0.95	1.93	2.860 (6)	166
O2—H2···O4*W*	0.95	1.56	2.499 (5)	171
O6—H6···O5*W*	0.84	1.79	2.600 (5)	162
O8—H8···O3^{v}	0.84	1.69	2.513 (4)	165
O12—H12···O3*W*^{viii}	0.84	1.76	2.596 (5)	171

Symmetry codes: (i) *x*, *y*, *z*−1; (ii) *x*, *y*, *z*+1; (v) −*x*, −*y*+1, −*z*+1; (vi) *x*, −*y*+1/2, *z*−1/2; (vii) −*x*+1, −*y*+1, −*z*+1; (viii) −*x*+1, −*y*+1, −*z*+2; (ix) −*x*+1, *y*+1/2, −*z*+3/2.